

# INTERPENETRATING POLYMER NETWORKS 279

Vol. 8

187. Y. Rotenberg, L. Horvka, and A. W. Neumann, *J. Colloid Interface Sci.* 93(1), 169 (1983).
188. A. F. Siegel, *Biometrika* 60, 242 (1982).
189. S. Wu, *J. Colloid Interface Sci.* 71, 605 (1979); erratum in *J. Colloid Interface Sci.* 73, 590 (1980).
190. H. W. Fox and W. A. Zisman, *J. Colloid Sci.* 6, 514 (1950); 7, 109, 428 (1952).
191. G. Porod, *Kolloid Z.* 124(2), 83 (1951); 125(1), 51 (1952); 125(2), 108 (1952).
192. J. T. Koberstein, B. Morra, and R. S. Stein, *J. Appl. Cryst.* 13, 34 (1980).
193. J. Letz, *J. Polym. Sci. Part A-2* 7, 1987 (1969).
194. F. P. Price, P. T. Gilmore, E. L. Thomas, and R. L. Laurence, *J. Polym. Sci. Polym. Symp.* 63, 33 (1978).
195. S. Kaplan and J. J. O'Malley, *Polymer* 22, 221 (1981).
196. L. W. Jelinski, J. J. Dumais, and A. K. Engel, *ACS Symp. Ser.* 247, 55 (1984).
197. J. J. Dumais, L. W. Jelinski, L. M. Leung, I. Gancarz, A. Galambos, and J. T. Koberstein, *Macromolecules* 18, 116 (1985).
198. S. R. Culler, H. Ishida, and J. L. Koenig, *Ann. Rev. Mater. Sci.* 13, 363 (1983).
199. D. T. Clark and W. J. Feast, eds., *Polymer Surfaces*, John Wiley & Sons, Inc., New York, 1978.
200. D. W. Dwight, T. J. Fabish, and H. R. Thomas, *ACS Symp. Ser.* 162 (1981).
201. D. Pan, *Bull. Am. Phys. Soc.* 30, 581 (1985).
202. J. M. Bloch, M. Sansone, F. Rondelez, D. G. Peiffer, P. Pincus, M. W. Kim, and P. M. Eisenberger, *Phys. Rev. Lett.* 54, 1039 (1985).

JEFFREY T. KOBERSTEIN  
The University of Connecticut

**INTERNALLY COLORED COPOLYMERS.** See COLORANTS; DYES,  
MACROMOLECULAR.

**INTERNAL PLASTICIZER.** See PLASTICIZERS

## INTERPENETRATING POLYMER NETWORKS

Synthesis, 284  
Morphology and glass transition, 296  
Physical properties, 318  
Applications, 329

An interpenetrating polymer network (IPN) is an intimate combination of two polymers both in network form, at least one of which is synthesized or cross-linked in the immediate presence of the other (1). Unlike chemical blends, there are no induced covalent bonds between the two polymers, ie, monomer A reacts only with other molecules of monomer A, as does B. A schematic representation of an ideal IPN is shown in Figure 1. In sequential synthesis, polymer A is swollen in the presence of monomer B and a cross-linking agent, and B is polymerized. In simultaneous synthesis, monomers A and B are cross-linked and polymerized by way of noninterfering modes. Thus, in addition to mechanical blending and copolymerization, IPNs represent a third mechanism by which different polymers can be physically combined.

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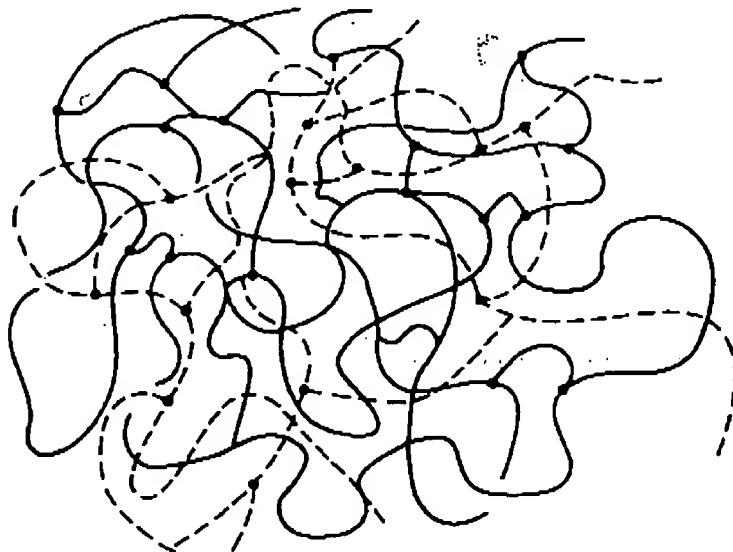


Fig. 1. Ideal interpenetrating polymer network (IPN): —, polymer A; ----, polymer B.

The chemical and physical combination of two or more structurally dissimilar polymers provides a convenient route for the modification of properties to meet specific needs. It facilitates processing and may impart flexibility, tensile and impact strength, chemical resistance, weatherability, flammability resistance, or other properties (2-4). The physical properties of the combined polymers depend on the properties of the polymers and the way they are combined.

Mechanical blending (Fig. 2a) is the traditional way of physically combining two or more polymers by mixing them in the liquid state, ie, melt, solution, or dispersion; there are no covalent bonds between the polymers (see POLYMER BLENDS). In chemical compositions, combinations, ie, two or more polymers or monomers, are combined by way of covalent bonds by random (Fig. 2b), block (Fig. 2c), alternate (Fig. 2d), or graft (Fig. 2e) copolymerization (see BLOCK COPOLYMERS; COPOLYMERIZATION; COPOLYMERS, ALTERNATING; and GRAFT COPOLYMERS).

The triblock copolymer shown in Figure 2c is the basis for thermoplastic elastomers, which behave as thermosets at use temperature, yet they flow and can thus be melt-processed at elevated temperatures. The physical cross-links imparted by hard domains over the soft segments classify these materials as thermoplastic IPNs (see ELASTOMERS, THERMOPLASTIC).

An IPN is distinguished from simple polymer blends, blocks, or grafts in two ways: it swells but does not dissolve in solvents, and creep and flow are suppressed (5).

In sequential interpenetrating polymerization, monomer I is combined with cross-linking agent and initiator to form network I. Network I is then swollen in monomer II containing cross-linking agent and initiator to form network II (Fig. 3a). Simultaneous interpenetrating networks (SINs) (Fig. 3b) are synthe-



Fig. 2. polymer; (c) b

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Vol. 8

Vol. 8

## INTERPENETRATING POLYMER NETWORKS

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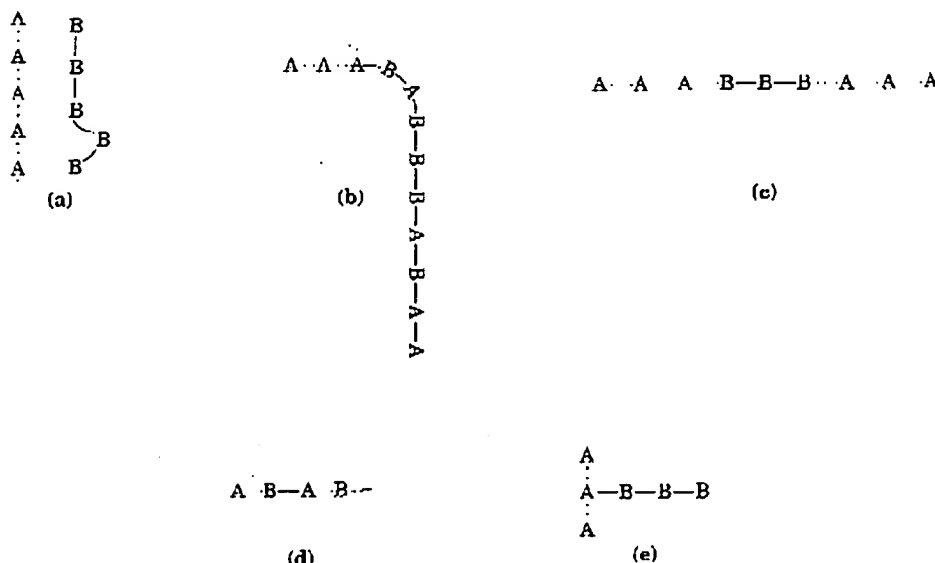


Fig. 2. Mixed polymer structures: (a) mechanical polymer blend; (b) random copolymer; (c) block copolymer; (d) alternating copolymer; (e) graft copolymer.

sized by combining monomers or linear prepolymers of the two monomers together with their respective cross-linking agents and catalysts, in bulk (melt), solution, or dispersion. The individual monomers are polymerized by chain or stepwise polymerization. Reaction between the polymers is usually prevented due to the different polymerization modes. If one of the two polymers is in network form (cross-linked) and the other a linear polymer, ie, not cross-linked, a semi-IPN results (Fig. 3c). If the polymerizations are sequential in time, four semi-IPNs may be distinguished (5). If polymer I is cross-linked and polymer II is linear, the product is called a semi-I IPN. If polymer I is linear and polymer II is cross-linked, a semi-II IPN results. For simultaneous polymerizations, only two semi-IPNs can be distinguished. The different categories of IPNs are shown in Table 1.

Interpenetrating polymerization is a mode of blending two or more polymers to produce a mixture in which phase separation is not as extensive as it would be otherwise. It is the only way of combining cross-linked polymers. Normal blending or mixing results in a multiphase morphology due to the well-known thermodynamic incompatibility of polymers (see COMPATIBILITY; MICROPHASE STRUCTURE). This incompatibility arises from the relatively small gain in entropy upon mixing the polymers due to contiguity restrictions imposed by their large chain length (7). However, if mixing takes place on a lower molecular weight level and polymerization is achieved simultaneously with cross-linking, phase separation may be kinetically controlled, since the entanglements have been made permanent by cross-linking. In other words, phase separation cannot occur without breaking covalent bonds.

Phase separation depends primarily on the compatibility of the polymers.

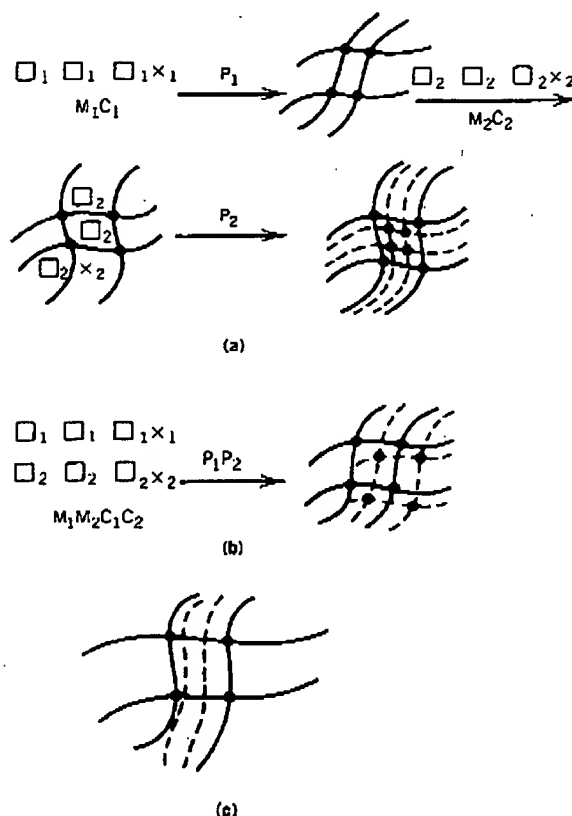


Fig. 8. Synthesis of IPNs (6): (a) sequential IPN; (b) simultaneous interpenetrating network (SIN); (c) semi-IPN. Network I, solid lines; network II, dotted lines: cross-link sites, filled circles. M = monomer; C = catalyst;  $\times$  = cross-linking agent; P = polymerization.

With highly incompatible polymers, the thermodynamics of phase separation is so powerful that it occurs before it can be prevented by cross-linking; mixing contributes little. With compatible polymers, phase separation is almost completely avoided. However, complete compatibility, which is almost impossible, is not necessary for complete phase mixing, i.e., interpenetration, since the permanent entanglements produced by interpenetration prevent phase separation. With moderate compatibility, intermediate and complex phase behavior results. Thus, IPNs with dispersed phase domains have been reported ranging from a few micrometers (the largest) (8) to a few hundred nanometers (intermediate) (9) to those without a resolvable domain structure (complete mixing) (10).

Interpenetrating polymer networks are a special example of topological isomerism (11) in macromolecules (12). Some permanent entanglements between the different cross-linked networks are inevitable in any intimate mixture of cross-linked networks. These are examples of catenation in polymer systems, i.e., different ways of embedding these molecules in three-dimensional space. Permanent entanglements constrain the motion of segments and simulate covalently bound chemical cross-links (13). Simplified theoretical models of such permanent

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Table 1. Classification of IPNs

Category	Definition
full IPN	any material containing two or more polymers in which there are no induced cross-links between the individual polymers
sequential IPN (SIPN)	polymer A is swollen in monomer B, its cross-linking agent, and initiator, polymerizing B <i>in situ</i>
simultaneous IPN (SIN)	monomers A and B, and their respective cross-linking agents and initiators, are polymerized simultaneously by way of noninterfering modes
thermoplastic IPN	a two-polymer IPN in which the individual polymers are thermoplastics; polymers may contain physical cross-links, eg, ionomers which join two or more chains together or may be phase-separated single polymer systems
semi-I IPN	sequential IPN in which polymer I is cross-linked and polymer II linear
semi-II IPN	sequential IPN in which polymer I is linear and polymer II cross-linked
pseudo-IPN	simultaneous IPN in which one polymer is in network form, ie, cross-linked, and the other linear

entanglements (14) exhibit a surprisingly large nonlinear elastic restoring force unlike that expected with chemical cross-links from ideal rubber elasticity theory.

Some thermoplastic IPNs contain physical cross-links within their polymer chains, joining two or more chains together; three types of physical cross-links can be readily identified (5): crystalline portions of a semicrystalline polymer, the glass or crystalline portion of a block copolymer, and the ionic portion of an ionomer. These materials often behave as thermosets at room temperature but as thermoplastics at elevated temperatures, since the physical cross-link can be broken by heat.

Combining polymeric networks in different compositions often results in controlled different morphologies and has produced IPNs with synergistic behavior. For example, a glassy polymer ( $T_g$  above RT) combined with an elastomeric polymer ( $T_g$  below RT), gives a reinforced rubber if the elastomer phase is

## 284 INTERPENETRATING POLYMER NETWORKS

Vol. 8

continuous and predominant, or a high impact plastic if the glassy phase is continuous (15). More complete phase mixing enhances mechanical properties owing to increased physical cross-link density. IPNs have been synthesized in various network compositions with optimum bulk properties such as tensile strength (16-24), impact strength (18,19), and thermal resistance (18-20,22), and minimal surface properties such as critical surface tension. Some of these synergistic IPN properties, such as the mechanical properties, reflect their special architecture. Others, such as thermal resistance, may result from the fact that IPNs are usually blends of different chemical types (25).

The IPN topology was long known and apparently rediscovered several times (26). Early patents were issued in the UK in the 1940s and in the United States in the 1950s. Staudinger and Hutchinson (27,28) described the production of smooth sheets of bulk-polymerized homopolymers, whereas others (29) used anionic and cationic IPNs as ion-exchange resins. The term IPN was first introduced in 1960 (30) in a study of homo-IPNs in which both polymer networks were composed of polystyrene cross-linked with divinylbenzene (DVB). A series of these IPNs was prepared by allowing the first cross-linked polystyrene network to absorb a calculated amount of a mixture of styrene and a 50% divinylbenzene-toluene solution containing catalyst, followed by the polymerization of the monomers within the original polymer network. A small increase in density of the resultant network was ascribed to interpenetration. The polystyrene-polystyrene IPNs were used as models for ion-exchange resins.

A study of the viscoelastic properties of such polystyrene homo-IPNs revealed no difference in density between a control polystyrene network and the IPN (31,32). However, cross-link densities in the IPNs were much higher. In addition to cross-link formation by chain transfer and extension of the original network, cross-link density was increased by entanglements. Rubber modulus was higher and swelling tendency lower; glass-transition temperature and the viscoelastic properties were not affected. Homo-IPNs were synthesized by several researchers (32-34).

The first IPN patent concerned a mixture of natural rubber, sulfur, and partly reacted phenol-formaldehyde (35); however, the term IPN was not applied.

**Synthesis****Sequential IPNs**

The term sequential refers to the time order of polymerization (Table 2). Polymer I and its multifunctional cross-linking agent, eg, divinylbenzene, are polymerized first. Polymer I is usually an elastomer because of its ease and rapidity of swelling. Above the  $T_g$ , extreme care must be taken to prevent solvent-type stress cracking. Monomer II is then swollen into the polymer I network and cross-linked via its initiator and corresponding cross-linking agents. The cross-link density in polymer I limits the extent of swelling.

**Poly(ethyl acrylate) With Polystyrene, Poly(methyl methacrylate), Poly(styrene-co-methyl methacrylate).** These IPNs can be synthesized via uv photopolymerization (24,36,37). The monomer, containing dissolved benzoin as the

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